

# MODELING THE LONG-TERM DEGRADATION OF A METALLIC WASTE FORM

T. H. Bauer  
Reactor Analysis & Engineering Division  
Argonne National Laboratory  
9700 S. Cass Ave.  
Argonne, IL 60439

S. G. Johnson  
Energy Technology Division  
Argonne National Laboratory  
P.O. Box 2528  
Idaho Falls, ID 83403

C. T. Snyder  
Chemical Technology Division  
Argonne National Laboratory  
9700 S. Cass Ave.  
Argonne, IL 60439

The submitted manuscript has been created by the University of Chicago as Operator of Argonne National Laboratory ("Argonne") under Contract No. W-31-109-ENG-38 with the U.S. Department of Energy. The U.S. Government retains for itself, and others acting on its behalf, a paid-up, nonexclusive, irrevocable worldwide license in said article to reproduce, prepare derivative works, distribute copies to the public, and perform publicly and display publicly, by or on behalf of the Government.

American Nuclear Society Fifth Topical Meeting  
DOE Spent Nuclear Fuel and Fissile Material Management  
September 17-20, 2002  
Charleston, South Carolina

# MODELING THE LONG-TERM DEGRADATION OF A METALLIC WASTE FORM

T. H. Bauer  
Reactor Analysis & Engineering Division  
Argonne National Laboratory  
9700 S. Cass Ave.  
Argonne, IL 60439

S. G. Johnson  
Energy Technology Division  
Argonne National Laboratory  
P.O. Box 2528  
Idaho Falls, ID 83403

C. T. Snyder  
Chemical Technology Division  
Argonne National Laboratory  
9700 S. Cass Ave.  
Argonne, IL 60439

## ABSTRACT

The principal aim of this effort is to develop models of long-term metal waste form (MWF) degradation that are credible, mechanistically based, and empirically calibrated. Utilizing new experimental data and analyses, this paper outlines an updated approach and summarizes the progress made.

The current modeling approach emphasizes the analysis of constituent release data from immersion tests. A significant amount of recently obtained immersion test data is described. Test solutions included both mild (well-water), and aggressive (high-chloride and strongly acidic) environments. In addition to predominant constituents Fe, Zr, Cr, and Ni, MWF test samples included: U, Pu, Tc, and Np.

Guided by analysis of new immersion test data, a mechanistic model has been developed that describes the time dependence of MWF corrosion leading to passivation. A common functional form relates MWF degradation from different passivating solution environments via scale factors for magnitude and passivation time.

Passivation is identified as the most important factor governing long-term durability, along with the long-term stability of oxide barrier layers that cause passivation. Experimental data demonstrated passivation behavior in nominal well water, concentrated well water, an aggressive high-chloride solution, but not in a strong acid.

Credible bounding estimates of long-term corrosion for nominal well water solution environments are based on fits to time dependence scaled by the measured release of uranium (empirically identified as the most efficiently released MWF constituent). These estimates involve no significant extrapolation beyond the data and time span of the present experiments. However, using the

mechanistic model, these estimates of corrosion and release could be lowered and/or extended to more aggressive solution environments (via scale factors) provided barrier layer stability can be assumed (or demonstrated) to persist for longer times.

## INTRODUCTION

A practical MWF has been under development for some time (~10 years) at ANL representing a mix of materials left behind in spent fuel cladding hulls following an electrorefining process [1]. Its predominant constituent is stainless steel (from cladding) plus 5-20 wt.% zirconium (fuel constituent), up to 10 wt.% residual heavy metals (e.g. U, Np and Pu), and some radioactive fission products at the 1-2 wt.% level (e.g., Ru, Re, Zr, Mo, Nb, Pd, and Tc). A MWF ingot is formed in a single process step by melting, alloying, and slowly cooling the constituents together within a high-temperature inert gas furnace. The resulting MWF is a mixture of Fe<sub>2</sub>Zr-type intermetallic phases and a stainless steel like iron solid solution phase. Fission product radionuclides are distributed throughout both types of phases, whereas U, Np and Pu reside principally within the intermetallics. Extensive development and testing of this MWF have demonstrated mechanical robustness and stable metallurgical phase structure as essential to its principal function of immobilizing hazardous radionuclide constituents [1].

A program of coordinated laboratory experimentation and analysis has also been underway to support credible long-term immobilization of radionuclides during storage in a geologic repository. While these present studies are necessarily short-term from a geological perspective, their aim is to (1) identify and quantify MWF degradation mechanisms and phenomena applicable to long-term analysis and (2) lead to models of long-term MWF degradation that are credible, mechanistically based, and empirically calibrated. An earlier status report of this

effort was presented in Ref. 2. Utilizing new experimental data and analyses, this paper outlines an updated approach and presents the progress made

## MODELING APPROACH

The predominant components of the MWF would be thermodynamically unstable in an oxidizing repository environment. Paradoxically, extensive experience gained over humanity's continuing "iron age" has shown that even reactive metals can be extraordinarily durable over a broad range of mild and even chemically aggressive environments. Mechanistically, degradation of the MWF proceeds through the formation of metal-oxide corrosion layers that cover and penetrate its surface. The basic oxidation/ reduction reactions of corrosion are components of electrochemical circuits driven by a "corrosion potential" established between the metal surface and the nearby solution environment. The more reactive the metal, the faster oxide layers develop. However, corrosion can be self-limiting or "passivated" should the metal-oxide layers, themselves, be mechanically adherent and impede the element transport needed to complete the circuit (The latter could occur if the layer were chemically impenetrable, and/or electrically insulating). In this fashion, high metallic reactivity can plausibly be associated with long-term durability.

For the MWF, such passivation is the key to long-term immobilization of radionuclides. A classical necessary condition for passivation is the existence of stable metal-oxide phases at the local corrosion potential. However, predicting the range of environments over which the multi-component, multi-phase MWF will passivate is neither straightforward nor practical. Thus, the corrosion performance of the MWF must be experimentally tested across the full range of repository relevant environments.

While a broad range of experimental techniques help identify and validate corrosion phenomena and mechanisms, direct measurement of penetration depth, corrosion front advance, and morphology is not straightforward. Practical quantitative estimation of MWF corrosion rates are currently based on information obtained through "immersion tests" of small samples.

Immersion tests of small "coupon" samples measure releases of elemental MWF constituents over time from samples immersed in a wide range of solution environments. Immersion testing represents a straightforward, but time-consuming, and

laboratory method for measuring uniform aqueous corrosion. Disadvantages include hard to control solution environments and high potential for contamination (all results of lengthy test intervals). Immersion test results may not be directly relevant to corrosion issues involving the mechanical strength of load bearing structures or even the integrity of containers. However, uniform aqueous corrosion is a major long-term degradation mode for large MWF ingots resting in a geological repository. In this case, constituent releases measured in immersion tests directly address issues of radionuclide immobilization and provide the on-average measures needed for its assessment.

Immersion test measurements are able to capture release rate evolution from initially high bare-metal values through rapid fall-off with the build-up of protective oxide layers. Measured constituent release is normalized by dividing constituent mass release by its weight fraction in the sample. (In tests where not all constituents are measured, total mass release may be estimated as the average of measured normalized releases "weighted" by constituent weight fraction.) Relative values of normalized release indicate the "efficiency" of releasing each constituent as the "corrosion front" of "altered" material advances into the metal. Constituents with low release efficiencies are strongly involved in the growth of stable oxide layers. However, the highest measured normalized loss rate among all constituents present may serve as a practical "marker" (greatest-lower-bound estimate) of the underlying corrosion rate itself.

## IMMERSION EXPERIMENTS

The earlier assessment of Ref. 2 made use of preliminary results from immersion tests of a limited number of MWF samples in nominal well water solutions. A more comprehensive program of immersion testing at ANL has since significantly expanded numbers of test samples and the range of solution types.

One ANL study [4] begun in the year 2000 tested multiple samples of simulated non-radioactive MWF samples for a total of 44 weeks in four 90°C solution environments ranging from mild to aggressive. The simulated MWF included major constituents and surrogates for fission products but no Tc, U, or other actinides. The four test solutions were: (1) SJ13- a simulated Yucca Mountain "J13" well water, (2) CJ13- a version of SJ13 concentrated by a factor ~100, (3) 10KCL, a high-chloride, 10,000 ppm NaCl solution, and (4) AJ13- a version of J13 acidified by the addition of HCl to pH=2. Five

samples were tested in each solution environment using identical Teflon vessels plus one “blank” vessel tested for a control. Three out of the five samples were polished to a one-micron finish and the remaining two were air-oxidized for two hours at 500°C. In all cases, the sample surface area to solution volume ratio (S/V) was  $\sim 10\text{m}^{-1}$ .

These experiments followed a “solution exchange” protocol in which both test solutions and vessels were replaced at regular intervals. Releases of MWF constituents from the samples over each interval (as found dissolved or precipitated in the test solution or plated out on the vessel inside surface) were measured during each interval and tracked. Measured background “releases” from the control blanks were subtracted. The solution exchange protocol efficiently tracks the time dependence of constituent release and maintains good control over the solution composition. However, the method is subject to data loss when measurements over a prescribed exchange interval fall below detection limits. It was for this reason that these experiments were terminated after 44 weeks.

A companion ANL study [3] tested a variety of radioactive MWF samples immersed in simulated J13 solution at 90°C from 1 to 13 weeks without solution

exchanges. While only one solution type was tested, these experiments featured radioactive samples from six representative MWF compositions containing: U, Pu, Tc, and Np. These actinide and fission product radionuclides, whose release from the MWF would be of significance to repository performance, were absent from the simulated MWF used in the first study. Cumulative releases of MWF constituents from the samples (as found dissolved in the test solution or plated out on the vessel inside surface) were measured following a preset test interval. A large number of samples were tested (all polished). Results at each reported time interval included (in many cases) 3 samples from each of 5 or 6 separate ingots. Tests were conducted in Teflon vessels where sample surface area to solution volume ratio (S/V) ranged from 10 to 40  $\text{m}^{-1}$ .

### TEST RESULTS

The following figures (1-3) indicate time-dependence and relative efficiency of constituent release from MWF samples into the various mild and aggressive test solutions used in the experiments. A log scale is used to capture the wide span of constituent normalized releases that were measured. Estimates of total (or weighted average) release are included in each case for reference. Measured

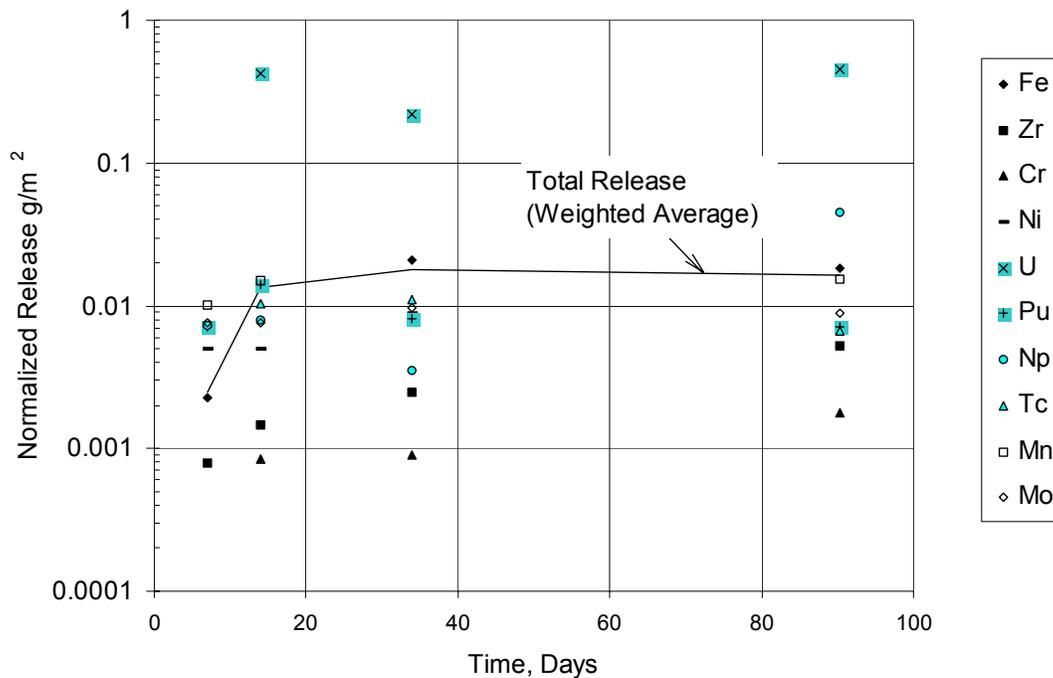


Fig. 1 Normalized Release from Radioactive MWF Samples into SJ13 Solution at 90C (Average over All Sample Compositions)

releases were often quite small and stochastic in nature. As many samples as possible were averaged to improve statistics. Except where systematic differences were noted, releases from the non-radioactive MWF averaged both polished and pre-oxidized samples. Data from the radioactive MWF averaged normalized releases from samples drawn from six different ingots.

Fig. 1 shows the sample-averaged measurements of cumulative normalized release from the radioactive ingots into 90°C simulated Yucca Mountain J-13 well water (SJ13). Allowing for extensive data scatter, normalized release measurements for the major MWF constituents from non-radioactive and radioactive samples were roughly consistent (within factors ~2).

Note that the normalized release of uranium shown in Fig. 1 is significantly higher than that of all other constituents and thus may “mark” the progress of an underlying corrosion front (as a “greatest lower bound”). By contrast, normalized releases of other radionuclides unique to the radioactive samples (Pu, Tc, and Np) are approximately at or below “average”. (The validity of the Fig. 1 uranium results is supported by a total of 16 test samples.) The cause of such highly efficient uranium release from the MWF in the face of passivating barrier layer growth is not

known. However, it may be associated with the well-documented instability of both uranium metal and oxide in an aqueous environment.

An underlying corrosion rate that is much greater than the total release rate implies that the vast majority of corrosion products remain part of stable metal-oxide layers. Consistent with this behavior, both experiments indicate leveling off of cumulative release, suggesting the growth of transport-limiting oxide barrier layers (passivation).

Figure 2 shows cumulative normalized release measurements from non-radioactive polished samples into a concentrated version of J-13 well water (CJ13). Because releases from polished samples were systematically higher than from oxidized samples, results were averaged separately. As in SJ13, measured time-dependence indicates passivation for both sample types. Total releases in CJ13, however, were similar to the SJ13 for oxidized samples but nearly 5 times higher for polished samples (Fig. 2).

Figure 3 shows sample-averaged cumulative normalized release measurements from non-radioactive samples into an aggressive high-chloride (10KCL) solution. As shown, the measured time-dependence indicates passivation, but at a level ~300

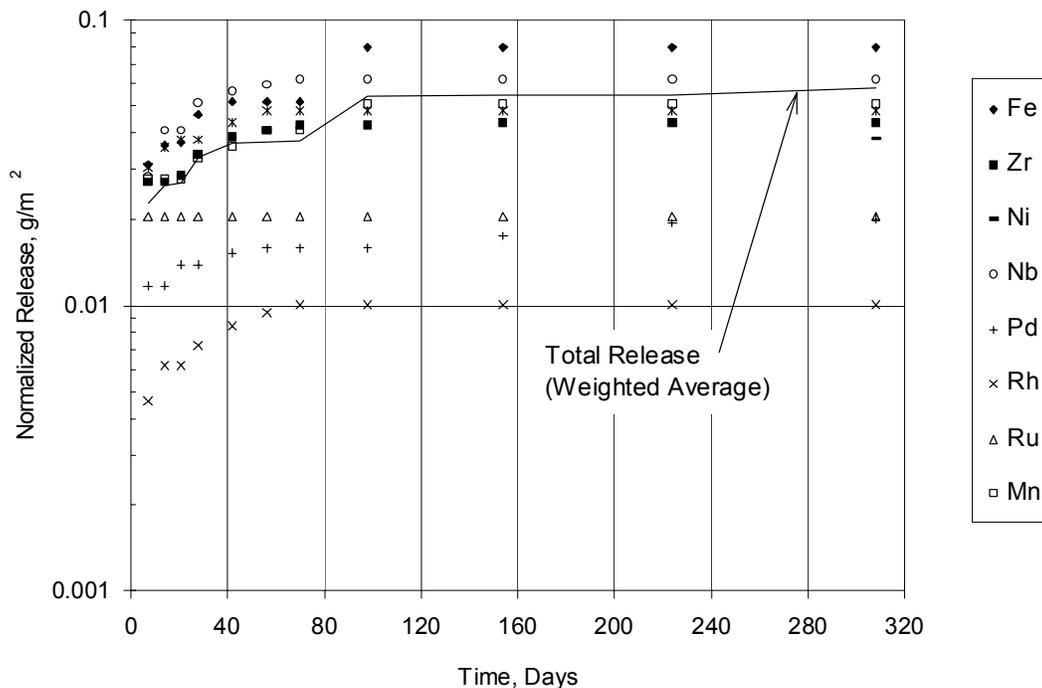


Fig. 2 Normalized Release from the Non-Radioactive MWF into CJ13 Solution at 90°C (Average of Initially polished Samples)

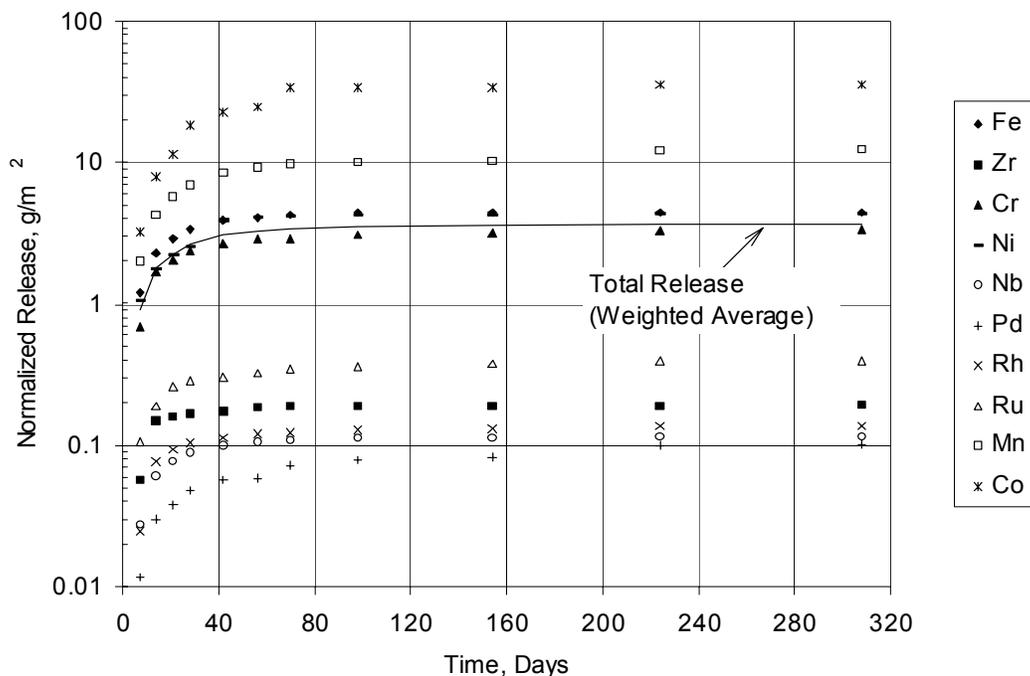


Fig. 3 Cumulative Normalized Release from the Non-Radioactive MWF into 10K Cl Solution at 90°C

times higher than into SJ13. On the other hand, measured releases into AJ13, the other aggressive pH=2 acidic solution tested, showed no sign of passivation and increased at a uniformly high rate with time.

It is instructive to compare and contrast patterns and orderings of normalized constituent releases and total (or weighted average) releases in Figs. 1-3. For example, in all cases total or weighted average release corresponds closely to the normalized release of Fe, the dominant MWF constituent. However, each test solution case shows a range of measured normalized constituent releases spanning a range of ~1-3 orders of magnitude, each with a distinct ordering of release efficiencies relative to the average. (Recall that relative values of normalized release yield relative efficiencies of release.) In fact, allowing for scatter in the data, both orderings and spacing on the log scale axis are approximately independent of time. The upshot of this conjecture is that, as corrosion proceeds, constituents are either retained or released with “efficiencies” that may vary by orders of magnitude but remain approximately independent of time.

### PROPOSED MECHANISM AND MODEL

The above observations from present testing can guide the development of a mechanistic model of

corrosion and constituent release, consistent with sound physical principles and a broad range of empirical knowledge. Overall, test results are consistent with the following modeling principles: (1) The transition between pure metal and stable oxide phases acts as a transport-limiting barrier layer. (2) As corrosion proceeds, constituents are either released “promptly” to the solution environment or added to the growing oxide layer. (3) In a given solution environment, the corrosion rate, constituent release rates, and layer growth rate are all proportional and fall off with time as a passivating barrier layer forms and grows.

Mathematically, in line with models found in the literature we may assume that corrosion and release rates fall off exponentially with barrier layer thickness [4] (consistent with a quantum tunneling mechanism). If the barrier layer thickness, itself, grows at a rate proportional to the corrosion rate, we may deduce that cumulative corrosion, release, or layer thickness will have the logarithmic time-dependence:  $a \ln(1 + b t)$ .  $t$  is exposure time,  $a$  is an overall normalization constant, and  $b^{-1}$  represents a characteristic passivation time.

In any case, the preceding analysis suggests that after both times and releases from all data sets plotted are appropriately scaled, observed passivation behavior should be consistent with a common

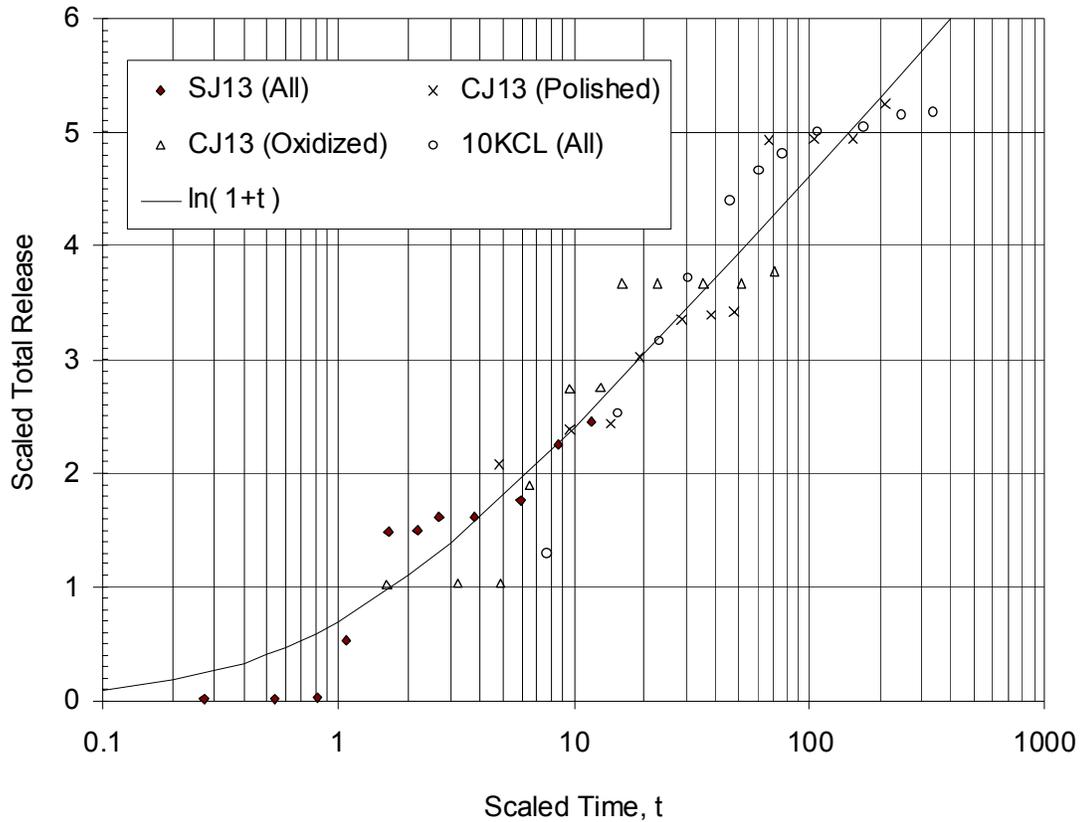


Fig. 4 Cumulative Release from Non-Radioactive Polished and Pre-Oxidized MWF Samples into Various Solutions at 90°C.

functional form. To illustrate this, scale factors for release and time were obtained for the solution/sample cases described above by fitting sample-averaged total release data to the above logarithmic form. “Normalizing” factors, listed in Table I, are  $a$  for release scale and  $b^{-1}$  for passivation time. Note that “passivation time” decreases and release scale increases with the aggressiveness of the test solution. Scaled releases and times are plotted on Fig. 4 in dimensionless form along with the function,  $\ln(1+t)$ . Release data from the aggressive AJ13 solution, which did not show evidence of passivation (i.e.,  $b \rightarrow 0$ ) is not included on Fig. 4.

### BOUNDING RELEASE MODELS

The above analyses of immersion test results suggest practical schemes for modeling long-term corrosion and radionuclide release rates. Scale factors, such as shown on Table I, provide a direct means of extrapolating releases from one solution environment to another. Results and discussion following Fig. 1b identified uranium release as (1) an upper bound to the normalized release of all other

radionuclides and (2) a potential marker for underlying corrosion. A scale factor for SJ13 “corrosion” may be estimated by using the fitted passivation time for non-radioactive SJ13 samples (Table I) and the logarithmic form to fit the limited number of uranium release measurements from Fig. 1. The result is included in Table I. Assuming further that the ratio of corrosion to total release will be greatest for the mildest solutions ( $\sim 70$  for SJ13), we may use this factor to bound corrosion scale factors in other more aggressive solutions where only releases are measured.

The most important factor governing long-term durability is passivation. Based on the preceding analysis, the most “optimistic” long-term projection assumes cumulative corrosion and release grow *logarithmically* with time. Should this be the case, degradation of the MWF effectively ceases, even for aggressive solution environments. (Corrosion rates drop off inversely with time, and total accumulation after  $10^6$  years would be  $\leq 6$  times that of the first year.)

Table I Normalizing Release Scale and Passivation Time

Test Solution (Measurement, Samples)	Time (days)	Release (g/m <sup>2</sup> )
SJ13 (Total release, all non-radioactive samples)	25.8	5.05x10 <sup>-3</sup>
SJ13 (Corrosion, all samples)	25.8	†3.55x10 <sup>-1</sup>
CJ13 (Total release, oxidized samples)	4.32	2.82x10 <sup>-3</sup>
CJ13 (Total release, polished samples)	1.46	1.09x10 <sup>-2</sup>
10KCL (Total release, all samples)	0.914	7.06x10 <sup>-1</sup>
† Estimated from normalized U release into SJ13		

However, the second most important factor governing long-term durability is barrier layer stability. The optimistic projection, assuming barrier layer growth depends only on corrosion rate, tacitly neglects two contingencies that may be important in the very long term: (1) slow dissolution of the oxide layer and (2) radically changing environmental conditions or mechanical disruption. In the first case, slow dissolution of the oxide layer would lead eventually to a steady state where corrosion and dissolution rates equalize [4]. In the second, a radical change in environment (even if consistent with passivation) or some mechanical failure could result in removal and subsequent rebuilding of the barrier layer. In this event, long-term cumulative corrosion and release would grow approximately linearly at rates given by averaging logarithmic growth over a time characteristic of environmental disruption.

The most pessimistic bounds to corrosion are obtained by assuming barrier layer stability only over the time span of the present experiments. Specifically, it is pessimistic to assume that long-term cumulative corrosion and release grow linearly

at the instantaneous rates determined at the end of the experiment. It is *extremely* pessimistic to assume that this linear rate is given by averaging logarithmic growth over the time span of the present experiment. (Such an assumption implies an unwarranted link between environmental contingencies and the short duration of an experimental program.)

Based on the preceding discussion, Table II lists bounding linear corrosion rates estimates using SJ13 test solution as a surrogate for nominal conditions in a flooded repository. (A single significant digit indicates the order-of-magnitude nature of the estimates.) Table II also includes a “spatial” penetration rate, based on an assumed MWF density of 7.65 g/cc. Other rates are shown on Table II for comparison. The total release rate measured in the AJ13 represents aggressive corrosion without passivation. A dissolution rate for borosilicate glass at 90°C in water (density 2.8 g/cc) provides some perspective with regard to degradation of other waste forms. (A more thorough approach for comparing the durability of different waste forms is presented in Ref. 5.)

Table II Bounding Corrosion Rates Deduced from Experimental Data

Solution Environment	Bounding Scenario	Rate (g/m <sup>2</sup> -y)	Penetration Rate (µm/y)
Nominal passivated (SJ13)	Instant. corrosion rate (308 days)	0.4	5 x 10 <sup>-2</sup>
	Average corrosion rate (308 days)	1	0.1
Aggressive (AJ13)	Measured release	6x10 <sup>2</sup>	7x10 <sup>1</sup>
Glass	Dissolution (water)	6	2

Using the mechanistic model (Fig. 4 and the scale factors of Table I), these estimates of corrosion and release could be lowered and/or extended to more aggressive solution environments. However, to do so requires extrapolation of measured release data and an assumption of barrier layer stability beyond 308-day span of the present experiments. We note that present immersion test data shows no evidence of barrier layer dissolution. (For the high-chloride,

10KCL an instantaneous corrosion rate similar to SJ13 would be expected after ~100 years.)

## CONCLUSIONS

Analyses of recent data from immersion tests of small MWF samples have advanced the development of credible models of long-term MWF degradation. A mechanistic model, based in large part on behaviors observed in the new experimental data, enables the time-dependence of corrosion and release for any solution environment and sample type to be fitted to a common functional form. Scale factors, such as shown in Table II, provide a direct means of relating measured releases from one solution environment to another.

Passivation behavior was experimentally demonstrated in nominal well water, concentrated well water, an aggressive high-chloride solution, but not in a strong acidic (pH=2) environment. In identifying the most important factors governing long-term durability, the first is passivation, and the second is barrier layer stability.

Credible empirically based bounding estimates of long-term constituent release for nominal well water solution environments are given in Table II. These are based in part on the measured release scale of uranium Table II estimates involve no significant extrapolation beyond the data and time span of the present experiments. Using the mechanistic model, these estimates of corrosion and release could be lowered and/or extended to more aggressive solution environments (via scale factors) provided barrier layer stability can be assumed (or demonstrated) to persist for longer times.

While uranium was identified empirically as the most efficiently released MWF constituent by an order of magnitude (Fig. 1), there is strong need to further validate and understand such "special" behavior. Direct examination of oxide layers would be very useful.

Additional ANL immersion tests are underway using uranium-bearing samples to quantify releases and establish MWF passivity over a range of temperature and pH environments relevant to a geological repository [6]. A number of immersion

tests have also been undisturbed for 2-3 years in SJ13 solutions. When terminated, these experiments may help validate barrier layer stability and other long-term aspects of the degradation model.

## ACKNOWLEDGEMENTS

(TBD)

This work was supported by the United States Department of Energy under contract W-31-109-ENG-38.

## REFERENCES

1. S. M. McDeavitt, "Preparation and Processing of the Metal Waste Form," in "Metal Waste Form Handbook," D. P. Abraham, ed., Argonne National Laboratory, ANL-NT-121 (June 1999), p1-1.
2. T. H. Bauer, D. P. Abraham, J. K. Fink, Irving Johnson, S. G. Johnson, and R. A. Wigeland, "Modeling Corrosion and Constituent Release from a Metal Waste Form," Proceedings of the 9th International High-Level Radioactive Waste Management Conference, Las Vegas, NV (April 29- May 3, 2001).
3. S. G. Johnson, M. Noy, T. DiSanto and T. L. Barber, "Release Of Neptunium, Plutonium, Uranium And Technetium From The Metallic Waste Form From The Electrometallurgical Treatment Process," Proceedings of the 2001 Fall Mtg of the Material Research Soc., paper JJ11.73, Boston, MA, Nov. 26-30, 2001.
4. D. D. Macdonald, "Passivity- the Key to Our Metal-Based Civilization," *Pure Appl. Chem.* 71, pp. 951-978 (1999).
5. T. H. Fanning, T. H. Bauer, E. E. Morris, and R. A. Wigeland, "A Generalized Definition for Waste Form Durability," (this conference) 2002.
6. W. L. Ebert, M. A. Lewis, T. L. Barber, and S. G. Johnson, "Accounting for EBR-II Metallic Waste Form Degradation in TSPA," (this conference) 2002.